Abstract: Adsorption of oxygen on Rh(111)[a)]

Patricia A. Thiel,[b)] J. T. Yates, Jr.,[c)] and W. H. Weinberg[d)]

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

(Received 21 September 1978; accepted 6 October 1978)

PACS numbers: 79.20.Fv, 82.65.My, 68.40. + e

The adsorption of oxygen on Rh(111) at approximately 100 K has been studied by thermal desorption mass spectrometry (TDS), Auger electron spectroscopy (AES), and low energy electron diffraction (LEED). Oxygen adsorbs in a disordered state at 100 K and orders irreversibly into an apparent (2 × 2) surface structure upon heating to $T \geq 150$ K. The kinetics of this ordering process have been measured by monitoring the intensity of the oxygen $(1,\overline{1/2})$ LEED beam as a function of time with a Faraday cup collector. The kinetic data fit a model in which the rate of ordering of oxygen atoms is proportional to the square of the concentration of disordered species due to the nature of adparticle interactions in building up an island structure. The kinetic data are shown in Fig. 1 for five temperatures at which the rate of ordering was measured, where $f(N_0)$ is the integrated form of the kinetic rate law. On the basis of these data, the activation energy for ordering is 13.5 ± 0.5 kcal/mol. This is consistent with values reported for oxygen ordering on Ir(111), 16–19 kcal/mol[1], and for oxygen migration on Ru, 14 kcal/mol.[2]

The Auger data and LEED intensity data of Fig. 2 show that at elevated temperatures, the oxygen undergoes a two-step irreversible disordering ($T \geq 280$ K) and dissolution ($T \geq 400$ K) process. The data shown in Fig. 2 were measured in the following way: Oxygen was adsorbed at $T \leq 120$ K, the surface was heated to the temperature indicated, and the intensity of the oxygen LEED beam, $I_{(1,\overline{1/2})}$, or the peak-to-peak amplitude of the differential 510 eV oxygen Auger transition, was recorded after the crystal had recooled. It was shown that the oxygen disorder → order → disorder transition of Fig. 2(A) is irreversible. Formation of the high-temperature disordered state is impeded at high oxygen coverages.

Oxygen thermal desorption spectra exhibited apparent second order behavior, with desorption beginning near 800 K at high coverage. Oxygen thermal desorption data and Auger data are presented in Fig. 3. It was shown that atomic oxygen and rhodium oxides do not desorb during thermal desorption of oxygen and hence cannot account for the lack of desorption of molecular oxygen at low oxygen exposures.

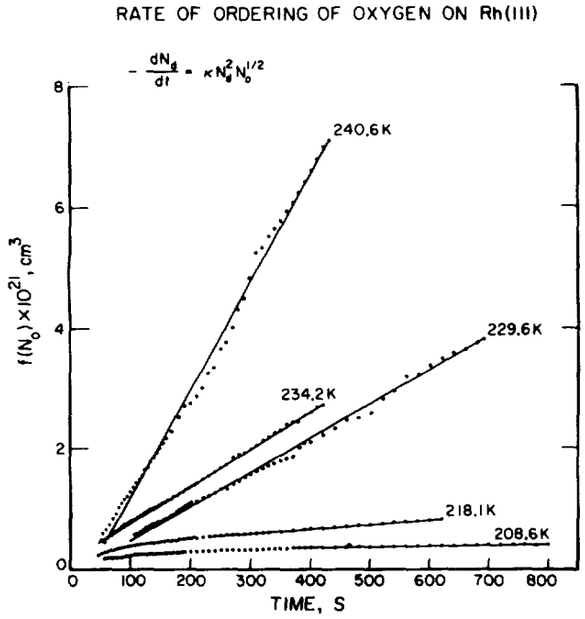

FIG. 1. Integrated form of the kinetic data as a function of time for the case in which the rate of ordering is equal to $\kappa N_\theta^2 N_0^{1/2}$. In calculating these values, it was assumed that $I_t = C' N_0^2$ where $C' = 3.49 \times 10^{-30}$ cm^4 for the normalized data, and I_t is the LEED beam intensity at time t. Thus,

$$f(N_0) = \frac{1}{C'^{3/4} N_\infty} \left\{ \frac{N_t^{1/2}}{N_\infty - N_t} - \frac{1}{2N_\infty^{1/2}} \ln \left[\frac{N_\infty^{1/2} - N_t^{1/2}}{N_\infty^{1/2} + N_t^{1/2}} \right] \right\}$$

where N_t = the value of N_0 at time t, and $N_\infty = 5.4 \times 10^{14}$ cm^{-2}.

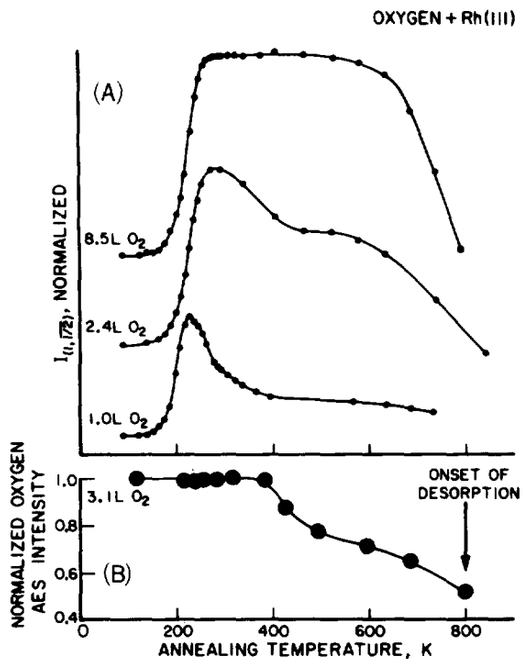

FIG. 2. Effects of the annealing on oxygen overlayer following adsorption at $T \leq 120$ K: (A) Intensity of oxygen $(1,\overline{1/2})$ beam as a function of annealing temperature; (B) Normalized value of the oxygen:rhodium Auger peak intensity ratio as a function of annealing temperature.

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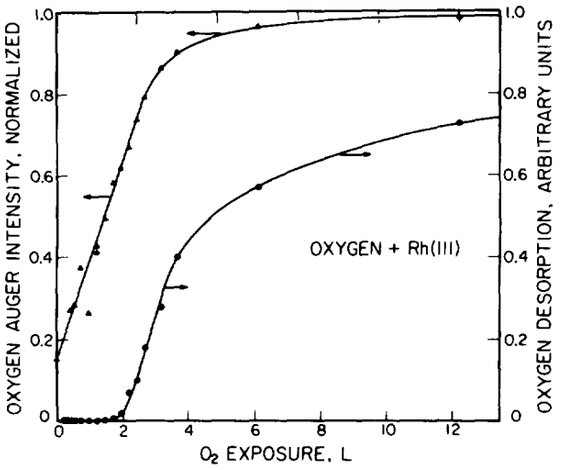

FIG. 3. Oxygen thermal desorption peak areas and oxygen differential Auger peak intensities (510 eV) as a function of O_2 exposure at $T \leq 170$ K.

On the basis of the Auger data of Fig. 2, at least 40% of the saturation coverage of oxygen must adsorb before O_2 desorption is observed. Thus, it appears that competition between two modes of oxygen depletion occurs during thermal desorption of oxygen: Dissolution into the bulk and desorption as molecular oxygen, with dissolution being the predominant depletion mode at low coverages. Conrad *et al.*[3] have also reported evidence for dissolution of oxygen into the bulk of Pd(111).

Analysis of the oxygen thermal desorption data, assuming second order kinetics, yields values of 56 ± 2 kcal/mol and 2.5×10^{-3} cm^2 s^{-1} for the activation energy of desorption and the preexponential factor of the desorption rate coefficient, respectively, in the limit of zero coverage. At nonzero coverages the desorption data are complicated by contributions from multiple states and/or interadsorbate interactions. A value for the initial sticking probability of 0.2 was determined from the Auger data shown in Fig. 3, where the constant rate of adsorption at exposures below 2 L implies a mobile precursor model for oxygen adsorption at $T \leq 170$ K.

Acknowledgment: Research was supported by the Army Research Office under Grant No. DAHC04-75-0170.

[a]Complete paper to appear in *Surface Science*.
[b]National Science Foundation Predoctoral Fellow.
[c]Sherman Fairchild Distinguished Scholar. Permanent Address: National Bureau of Standards, Washington, D.C. 20234.
[d]Alfred P. Sloan Foundation Fellow, and Camille and Henry Dreyfus Foundation Teacher-Scholar.

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Abstract: Chemisorption of oxygen on the (110) surface of iridium

D. E. Ibbotson, J. L. Taylor,[a] and W. H. Weinberg[b]

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

(Received 27 September 1978; accepted 6 November 1978)

PACS numbers: 82.65.My, 82.65.Jv, 73.40.Cg, 61.14.Hg

The chemisorption of oxygen on Ir(110) has been investigated under ultrahigh vacuum conditions with thermal desorption mass spectrometry (TDS), contact potential difference measurements, Auger electron spectroscopy, and LEED. Oxygen may adsorb in three distinct chemical states: a molecularly chemisorbed species that is stable below 100 K, a dissociatively chemisorbed species, and a surface oxide that forms rapidly above 700 K.

The oxide layer saturates at a coverage of 0.25 ML (1 ML = 9.6×10^{14} atoms/cm^2) and forms with an estimated activation energy of 45 kcal/mol, assuming first order kinetics and a preexponential factor of 10^{13} s^{-1}. Two forms of the surface oxide are observed, a disordered phase and an ordered phase which corresponds to a (1 × 4) LEED pattern. Both forms exhibit identical chemical properties. Formation of the oxide layer through thermal activation causes the total saturation coverage to increase from 1 ML on the clean surface to 1.25 ML on the oxidized surface, as evidenced from TDS.

Different LEED patterns of dissociatively chemisorbed oxygen are observed on clean and oxidized Ir(110). A $p(2 \times 2)$ structure forms on the clean surface near 0.25 ML coverage, whereas a $c(2 \times 2)$ structure forms on the oxidized surface near 0.5 ML. Thermal annealing is necessary to order the $c(2 \times 2)$ in the [001] azimuth with an energy of diffusion of 47 kcal/mol, assuming first order kinetics and a preexponential factor of 10^{12} s^{-1}. Slow ordering of the $p(2 \times 2)$ in the [001] azimuth at 300 K is observed on the clean surface with an estimated diffusional energy of 20 kcal/mol, again assuming the same kinetics as above.

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